Oligomeric Polymer Surfactant Driven Self-Assembly of Phenylene-Bridged Mesoporous Materials and Their Physicochemical Properties

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The detailed synthesis of highly hydrophobic average pore benzene-bridged hybrid mesoporous silicas under an acidic medium is described. With the use of a 1,4-bis(triethoxysilyl)benzene silsesquioxane precursor and biodegradable alkyl polyoxyethylene (Brij-56 or Brij-76) nonionic surfactogomers as supramolecular templates, no molecular scale periodicity was observed. The well-defined mesoporous materials could be synthesized with two-dimensional hexagonal (p6mm) symmetries. The textural and surface properties (adsorption isotherms of water and benzene vapors) were estimated and were compared to the analogous benzene-bridged mesoporous silica with molecular scale periodicity which was prepared using cationic surfactant under basic conditions. Different textural properties resulted for the two kinds of materials and revealed some important insights regarding the structure and nature of the materials.

Introduction

Hybrid mesoporous materials have gained much interest in recent years, because of the possibility of tailoring the pore structure, framework composition, and morphologies over a wide range.1,2 The synthesis of highly hydrophobic mesoporous structures using a supramolecular self-assembly approach is particularly of high commercial interest because of the variety of unique possibilities, such as immobilization and encapsulation of large molecules.1–3 During the last 4 years, significant progress has been made in the field of mesoporous organosilicas allowing controlled design of solids carrying inorganic, organic, and useful biofunctionalities. MCM-41 type ethane-bridged mesoporous organosilicas was the first to be studied. Several synthetic strategies have already been proposed for the synthesis of ethane-bridged mesoporous organosilicas starting with alkytrimethyl-
acid functionalized mesoporous material from the meso-
porous benzene–silica possessing mercapto propyl (–CH₂-
SH) groups via oxidative transformation of the thiol (–SH)
to the sulfonic (–SO₃H) group. In another very recent
development, the synthesis of mesoporous benzene–silica
with large pores ranging from 6.0 to 7.4 nm in diameter
using a triblock copolymer surfactant was disclosed. Overall,
the number of reports on the corresponding benzene-bridged mesoporous hybrid materials are very limited.

In this article, we report the detailed synthesis of
average-pore benzene-bridged mesoporous materials in
the presence of nontoxic and biodegradable Brij-56
[C₃H₅₃(OCH₂CH₂)₃OH] and Brij-76 [C₃H₅₃(OCH₂CH₂)₁₀-
OH] oligomers as a surfactant under acidic conditions.
The study describes the mesophases and architectural
controls in the organic–inorganic hybrid system induced
by the variation in the templating media. The synthetic
route produces high-quality benzene–silica hybrid
mesoporous materials, and an acidic route allows the control
in the design of organosilica framework due to weaker
inorganic–organic interaction. Also, the comprehensive
structural and surface properties are compared to the
mesoporous benzene–silica hybrid materials prepared
using cationic surfactant under basic conditions.

Experimental Section

Materials. The nonionic surfactants Brij-56 and Brij-76
are the polyoxyethylene derivatives of alkyl ether [C₈H₁₇EO]₁₀; Aldrich Chemicals] and were used without further purification. The two
surfactants have the same hydrophilic group but different alkyl
groups. High-purity 1,4-bis(triethoxysilyl)benzene (BTEB) pre-
cursor (supplied by Azmax) was used. Hydrochloric acid (2 N)
and ethanol were purchased from Wako Chemicals.

Synthetic Procedures. In a typical synthetic procedure, 2.3 g
of Brij-56 surfactant was first dissolved in 6.1 g of deionized
water and 31 g of 2 N HCl solution by stirring and heating at
70 °C, and then 2.06 g of BTEB precursor was added to the
homogeneous solution under vigorous stirring at the same
temperature and stirring was continued for 4 h. The suspension
was cooled and stirred for 14 h at ambient temperature, followed
by further heating with continued stirring at 70 °C for another
2 h. The white solid product was then recovered by filtration,
washed thoroughly with a copious amount of deionized water,
and dried under a vacuum at ambient temperature (~74% yield).
The surfactant was then removed by solvent extraction using
0.75 g of as-made material in 150 mL of ethanol and 3.1 g of 2
N HCl solution at 60 °C for 6 h (~57% yield after extraction).
In the case of the Brij-76 surfactant, the 1.69 g of surfactant
was added to the deionized water and completely dissolved by
stirring the solution for several hours at 70 °C, and then 2.0 g
of the BTEB precursor was added dropwise to the solution.
The gel mixture was stirred for 8 h at 70 °C and left for 24 h of stirring
at ambient temperature. The remaining procedure and treatment
were the same as described above for the material prepared using
Brij-56 as the surfactant.

The materials were also subjected to hydrothermal stabilization.
The material (50 mg) suspension in distilled water (30 g)
was kept in an airtight glass bottle at 90 °C for 24 h. Powder X-ray
diffraction (PXRD) and nitrogen adsorption measurements. Effect
of the calcination temperature on the mesostructures was also
analyzed.

Characterization. The PXRD patterns were measured on a
Rigaku RINT-2200 diffractometer with Cu Kα radiation (40 kV
and 30 mA) from 1° to 40°, 0.01 step, and 1° 20/min scan speed.

The porosimetry measurements (N₂ isotherms) were obtained
on Quantachrome Autosorb-1 sorptometer at ~196 °C. Prior to
measurement, all samples were outgassed at 80 °C at 10⁻⁶ Torr.
The Brunauer–Emmett–Teller (BET) surface areas were cal-
culated from the linear part of the BET plot (P/P₀ = 0.05–0.3).
Pure size distributions were determined using the Barrett–
Joyner–Halenda (BJH) and density functional theory (DFT)
models from the adsorption branch of the isotherms.

31C cross-polarization (CP) and ²⁹Si magic-angle spinning
(MAS) NMR spectra were recorded on a Bruker MSL-300WB
spectrometer at 75.47 and 59.62 MHz for ¹³C and ²⁹Si NMR,
respectively, using 7-mm zirconia rotors and a sample spinning
frequency of 3 kHz. The chemical shifts for all the spectra were
referenced to tetramethylsilane at 0 ppm.

The adsorption isotherms of water and benzene vapors were
obtained using an automatic vapor adsorption apparatus, BEL-
SORP-18, BEL Japan, Inc. Prior to measurements all samples
were evacuated at room temperature below 2 × 10⁻⁸ mmHg.
Water and benzene adsorption isotherms were measured for the
surfactant-free and subsequently calcined materials.

Thermogravimetric analysis (TGA) was performed using a
Rigaku Thermo PlusTG-8120 instrument with a program rate
of 10 °C min⁻¹ in air as well as in the nitrogen atmosphere with
a flow rate of 500 mL min⁻¹.

Results and Discussion

Mesostructure Formation and Their Stabilization. The PXRD patterns (Figure 1) for as-synthesized
benzene-bridged organosilicas (B56-1 and B76-1) prepared
from Brij-56 and Brij-76 surfactants exhibit strong reflections
at 2₀ = 1.69° (d₁₀₀ spacing = 5.22 nm) and 2₀ = 1.73°
(d₁₀₀ spacing = 5.10 nm), respectively. The surfactant-
free organosilicas (B56-2 and B76-2) revealed well-defined
patterns with three diffraction peaks in the low angle
region (2θ < 5°), which are assigned to (100), (110),
and (200) with two-dimensional hexagonal (p6mm) symmetry.
The PXRD peak (d₁₀₀) for surfactant-free material after
the solvent extraction (Figure 1b) was significantly
increased in intensity, no considerable shrinkage in the
lattice spacing was noticed after surfactant removal (see
the tables), and the d spacings were 5.04 and 5.01 nm for
the Brij-56 and Brij-76 derived materials, respectively.
Furthermore, the intensities were considerably improved upon
by hydrothermal stabilization (B56-3 and B76-3) indicating substantial framework ordering relative to the parent materials (Figure 1c). The materials retained their mesoporous character after calcinations (B56-4; B56-5 and B76-4; B76-5). The greater improvement in intensity upon calcinations is likely in these materials, although the reasonable lattice contractions were observed with respect to as-synthesized materials (Figure 2a). The lattice contractions increased with increasing calcination temperature. The detailed crystallographic properties along with textural properties are also summarized in Tables 1 and 2 for mesoporous materials derived from Brij-56 and Brij-76 surfactants, respectively.

No molecular scale periodicity was observed, unlike reported for the mesoporous benzene–silica prepared using cationic surfactant under basic conditions. It can be postulated that unlike the cationic surfactant the nonionic surfactant does not exert electrostatic attraction but possibly penetrates into the hydrophobic and palisade regions, thereby inducing a structural arrangement without any molecular scale periodicity in the pore walls. The optimization of the interface charge density matching and surfactant packing is likely to impede the complete cross-linking of the silica network and allows efficient structuring to two-dimensional hexagonal mesophases. Therefore, the resultant material remained essentially texturally and chemically indistinguishable from benzene–silica mesoporous materials reported with the molecular scale periodicity. Sayari et al. showed the formation of small molecular scale periodicity in the pore walls using transmission electron microscopy (TEM) measurements; however, they failed to observe the periodicity using the X-ray diffraction.16

Although we have succeeded in the formation of more highly ordered mesoporous materials than reported earlier, we do not have any evidence of the molecular scale periodicity. Further, the TEM images of both mesostructured materials derived from Brij-56 and Brij-76 surfactants are presented in Figure 3. In support of the PXRD observation, the TEM images taken showed the uniformity of both the materials and provide direct evidence for the presence of ordered hexagonal arrays aligned in the one-dimensional channel. These are also similar to those previously reported for benzene-bridged silica.12–15

Scanning electron microscopy (SEM) images with higher resolution shown in Figure 4 depict that both the materials form particle clusters of about 2 μm.

**Porosimetry Studies.** Nitrogen adsorption isotherm of type IV, with a sharp increase in the adsorption at P/P0 = 0.35–0.45 due to capillary condensation, clearly indicates that surfactant-free materials have a uniform mesoporous structure. The DFT pore diameter (NLDFT equilibrium model), BET surface area, and pore volume were 4.6 nm, 1182 m² g⁻¹, and 0.87 cm³ g⁻¹ and 4.3 nm, 932 m² g⁻¹, and 0.65 cm³ g⁻¹ for the surfactant-free materials derived from Brij-56 and Brij-76 surfactants, respectively (Figure 5). While for the hydrothermally stabilized materials the DFT pore diameter, BET surface area, and pore volume were 4.3 nm, 1469 m² g⁻¹, and 1.19 cm³ g⁻¹ and 3.5 nm, 1107 m² g⁻¹, and 1.17 cm³ g⁻¹ for the Brij-56 and Brij-76 surfactant derived materials, respec-

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**Table 1. Textural Properties of Mesoporous Benzene–Silica Derived by Brij-56 Surfactant**

<table>
<thead>
<tr>
<th>entry no.</th>
<th>material description</th>
<th>lattice spacing a, nm</th>
<th>S_BET, m² g⁻¹</th>
<th>D_p,DFT, nm</th>
<th>V_p, cm³ g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>B56-1</td>
<td>as -synthesized</td>
<td>6.03</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>B56-2</td>
<td>solvent-extracted, surfactant-free</td>
<td>5.82</td>
<td>1182</td>
<td>4.6</td>
<td>0.87</td>
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<tr>
<td>B56-3</td>
<td>hydrothermally stabilized prior to surfactant removal</td>
<td>5.89</td>
<td>1469</td>
<td>4.3</td>
<td>1.19</td>
</tr>
<tr>
<td>B56-4</td>
<td>calcined at 250 °C after surfactant removal</td>
<td>5.49</td>
<td>1189</td>
<td>4.3</td>
<td>0.91</td>
</tr>
<tr>
<td>B56-5</td>
<td>calcined at 400 °C after surfactant removal</td>
<td>5.31</td>
<td>1194</td>
<td>4.3</td>
<td>0.91</td>
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</table>

**Table 2. Textural Properties of Mesoporous Benzene–Silica Derived by Brij-76 Surfactant**

<table>
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<tr>
<th>entry no.</th>
<th>material description</th>
<th>lattice spacing a, nm</th>
<th>S_BET, m² g⁻¹</th>
<th>D_p,DFT, nm</th>
<th>V_p, cm³ g⁻¹</th>
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<td>B76-1</td>
<td>as synthesized</td>
<td>5.89</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
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<td>B76-2</td>
<td>solvent-extracted, surfactant-free</td>
<td>5.78</td>
<td>932</td>
<td>4.3</td>
<td>0.65</td>
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<td>B76-3</td>
<td>hydrothermally stabilized prior to surfactant removal</td>
<td>5.87</td>
<td>1107</td>
<td>3.5</td>
<td>1.17</td>
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<tr>
<td>B76-4</td>
<td>calcined at 250 °C after surfactant removal</td>
<td>5.81</td>
<td>955</td>
<td>4.1</td>
<td>0.69</td>
</tr>
<tr>
<td>B76-5</td>
<td>calcined at 400 °C after surfactant removal</td>
<td>5.60</td>
<td>963</td>
<td>4.1</td>
<td>0.70</td>
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</tbody>
</table>

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**Figure 2.** X-ray diffraction profiles for mesoporous hybrid benzene–silicas derived from (A) Brij-56 and (B) Brij-76 surfactants. (a) B56-4 or B76-4 (extracted followed by calcined at 250 °C) and (b) B56-5 or B76-5 (direct calcination at 400 °C).

**Figure 3.** TEM images for surfactant-free (a) B56-2 and (b) B76-2 mesoporous hybrid benzene–silicas derived from Brij-56 and Brij-76 surfactants.
Figure 4. SEM images for surfactant-free (a) B56-2 and (b) B76-2 mesoporous hybrid benzene–silica derived from Brij-56 and Brij-76 surfactants.

Figure 5. Nitrogen adsorption isotherms and BJH pore-size distribution curves (inset) for surfactant-free (a) B56-2 and (b) B76-2 mesoporous benzene–silica derived from Brij-56 and Brij-76 surfactants.

Figure 6. Nitrogen adsorption isotherms and BJH pore-size distribution curves (inset) for hydrothermally stabilized (a) B56-3 and (b) B76-3 mesoporous benzene–silica derived from Brij-56 and Brij-76 surfactants.

NMR Studies and Structure Confirmation. The $^{29}$Si MAS NMR of both organosilicas derived from Brij-56 and Brij-76 surfactants showed similar spectra. Three signals at $-63.2$, $-70.5$, and $-79.6$ ppm for Brij-56 derived material and at $-63.5$, $-71.0$, and $-79.7$ ppm for Brij-76 derived material are assigned to Si species covalently bonded to the carbon atom of $^{T1}[Si(C(OH)2(OSi)]$, $^{T2}[SiC-OH(OSi)2]$, and $^{T3}[SiC(OH)(OSi)3]$, respectively (Figure 7). To be consistent with the above, no signals due to SiO$_4$ species ($Q^0$, $n = 1–4$) were observed, indicating that complete cross-linking occurred in the materials. The $^{T2}$/

Figure 7. $^{29}$Si MAS NMR spectra for surfactant-free mesoporous benzene–silica derived from (a) Brij-56 and (b) Brij-76 surfactants. (A) B56-2 and B76-2 (solvent-extracted); (B) B56-3 and B76-3 (after hydrothermal stabilization followed by solvent extraction).

Figure 8. $^{13}$C MAS NMR spectra for surfactant-free mesoporous benzene–silica after hydrothermal stabilization followed by solvent extraction (B56-3 and B76-3) derived from (a) Brij-56 and (b) Brij-76 surfactants. $T^2$ peak intensity ratios were 0.48 and 0.51 for Brij-56 and Brij-76 derived materials, respectively, which are much lower than those observed for mesoporous benzene–silica prepared from cationic and triblock copolymer surfactant.

The $^{13}$C CP-MAS NMR spectra of both the surfactant-free organosilicas, derived from Brij-56 and Brij-76 surfactants, revealed that the framework is a covalently bonded network of O$_{1.5}$–Si–C$_6$H$_4$–Si–O$_{1.5}$ units. The occurrence of a large peak at about 133.7 ppm along with sidebands (denoted with asterisks) is attributed to the phenylene group connected to Si (Figure 8).

Thermal Stability. In addition, these materials exhibited thermal stability comparable to those of mesoporous benzene–silica derived from the triblock copolymer and cationic surfactant. Thermogravimetric curves (TGA and thermal gravimetric analysis, DTA) in air and nitrogen environments for synthesized mesoporous hybrid benzene–silicas derived from Brij-56 and Brij-76 surfactants are shown in Figure 9. Below 100 °C, the weight loss

The hysteresis obtained for the individual sorption mechanism is due to residual water adsorbed in the samples, while a further loss in the range of 100–550 °C corresponds mainly to the thermal decomposition of surfactant and probably a small amount of the matrix of bridged phenylene. The weight loss in the range of 550–800 °C can be attributed to the decomposition of the phenylene group bridged to the framework. The weight loss was higher in the air environment compared to that in the nitrogen environment. Both materials showed similar trends in the air as well as nitrogen atmospheres.

Further, the surfactant-free materials, obtained after hydrothermal stabilization and subsequent extraction and calcinations at 400 °C of the synthesized material, showed a sharp weight loss only in the temperature range 550–700 °C due to loss of benzene moieties. Absolutely no weight loss in the lower region clearly indicates that the surfactant was completely removed from the materials (Figure 10).

**Effect of Pore-Wall Structure on the Surface Properties.** A comparative study of water and benzene adsorption on the set of ordered benzene-bridged hybrid mesoporous materials derived from oligomeric surfactant (Brij-56) and cationic surfactant (C_{18}TMACl) was done. The surface and framework hydrophobicities are two separate orientation factors which describe the entirely different mesostructural behavior of these two types of benzene-bridged mesoporous materials. The hydrophobic nature of the materials was evaluated by adsorption–desorption isotherm measurements for both water as well as benzene vapors and is discussed in terms of adsorption hysteresis obtained for the individual sorption mechanism.

The details on the adsorption procedural methods are already outlined in the experimental section.

The water adsorption isotherms (Figure 11) showed unusual type V in the IUPAC classification, which have never been observed for the other adsorbates such as nitrogen, oxygen, argon, and so forth. The adsorption branch of the isotherm obtained for the B56-2 sample (solvent-extracted) showed a rapid increase at low pressure, a characteristic of reasonable adsorbent–substrate interaction usually seen for the hydrophilic silica surfaces. The adsorbed water monolayer was reached at a relative pressure (P/P₀) of 0.3, and the quick rise in the adsorption after this pressure is related to capillary condensation in the mesopores of the material. The B56-5 sample (calcined at 400 °C) showed a somewhat similar water vapor adsorption isotherm especially at low pressure where water–silica interaction was not so dominant. This also describes the partial depletion in the hydrophilic nature of the surface of the material with lower hydroxyl surface density after calcinations. This is perhaps due to the removal of hydrogen-bonded hydroxyl groups while isolated hydroxyl groups remained intact upon calcinations.

However, the correlation between affinity to water and hydroxyl surface density is not straightforward. Also, the calcined material also showed similar affinity for the water, and the monolayer of adsorbed water could be reached at a relative pressure of 0.41. The slope of the isotherm showed a continuous increase in the amount of water adsorbed, prior to capillary condensation. Similar trends are already reported for FSM 16 type materials\(^\text{17}\) where the amount of monolayer water adsorption was almost double at similar relative pressures. This evidently confirms that materials studied in this report are non-porous in nature.

Despite having similar hydrophobic (benzene) densities, the extracted and calcined material showed different hysteresis; thus, it is meaningful to compare the water adsorption at a fixed relative pressure value normalized to the surface area for the inspection of molecular configuration of adsorbed water on these mesoporous materials. This could explain the variation in the local water density over the surface with some accumulation of molecules in the most accessible hydrophilic portion of the material with highest hydroxyl surface density. This could also clearly support the observation of the confinement-induced capillary condensation that is expected to happen at pressures lower than saturation pressure in the mesoporous materials. This can be probably assigned to the change in the contact angle between surface and water due to the possible lattice shrinkage. Similarly, the

These results also reveal that the affinity of benzene to adsorption was 0.76 cm$^3$ g$^{-1}$. The total pore volume calculated on the basis of benzene packing density of benzene is an important factor to conclude about its behavior of benzene adsorption. The monolayer adsorption of benzene was faster, and the isotherm exhibits a steep increase in adsorption after the site radial distribution function in the structure of the monolayer water strongly influences the silica–water interactions.

Additionally, the benzene adsorption isotherms provide more insight on the pore wall structure of the materials. The benzene adsorption isotherms (Figure 13) of the surfactant-free B56-2 (solvent-extracted) sample also showed type IV shape isotherms in IUPAC classification. The monolayer adsorption of benzene was faster, and the isotherm exhibits a steep increase in adsorption after relative pressure equal to 0.16 due to rapid filling of benzene in mesopores. Because the hydrophobic benzene moieties are randomly distributed in the materials, the packing density of benzene is an important factor to conclude about its behavior of benzene adsorption. The total pore volume calculated on the basis of benzene adsorption was 0.76 cm$^3$ g$^{-1}$, that is, slightly lower than those estimated by nitrogen adsorption (0.87 cm$^3$ g$^{-1}$). These results also reveal that the affinity of benzene to the surface was lowered as a result of lower hydroxyl group density and π–π stacking of benzene on the surface.

In the case of the similar water adsorption experiments conducted on the benzene–silica with molecular scale periodicity in the pore walls (derived from the cationic templating route in basic medium), the effect of calcination on the water vapor adsorption was negligible (Figure 12). This clearly indicates that the surface properties of both materials derived using oligomeric and cationic surfactants are largely different. The surface curvature is expected to play a vital role in this case. The crystal-like pore walls of the materials perhaps modify the isosteric heat of absorption and lower the local curvature that eventually regulates the interaction properties of water with the silica surface. The water monolayer of the surface was reached at a relative pressure equal to 0.46, which explains that the isosteric heat of adsorption value might reach very close or below the heat of liquefaction of bulk water, a signature of their hydrophobic character. Also, the results unambiguously explain that the hydrophobic character of the surface pore walls also includes a locally very unfavorable arrangement of hydroxyl groups, which minimize the number of hydrogens bonding rather than simply reduce the surface hydroxyl density. Additionally, the site–site radial distribution function in the structure of the monolayer water strongly influences the silica–water interactions.

On the other hand, the benzene adsorption–desorption isotherm obtained for the benzene–silica hybrid mesoporous materials having molecular scale periodicity in the pore walls showed no significant difference in the nature of the benzene adsorption and the capillary condensation step (Figure 14a). However, the total amount of benzene adsorbed was reduced and exhibits a steep increase in adsorption after a relative pressure equal to 0.20. This suggests that the structural organization of the materials preferentially contributes to the surface properties. The amorphous pores of the benzene–silica mesoporous materials derived from Brij-56 surfactant may be relatively less hydrophobic in nature as a result of the random distribution of benzene moieties compared to benzene–silica with molecular scale periodicity where the benzene moieties are homogeneously distributed in the crystal-like pore walls.

The comparison plot shown in Figure 15 provides more insights regarding the involvement of structural arrangements in the textural properties of the materials. The comparison plot was made taking the benzene adsorption data on the mesoporous benzene–silica with molecular scale periodicity as a standard. No significant deviation was observed, and the curve showed the deviated linearity also passing through the origin. The adsorption for the unit surface area is greater for the materials with amorphous pore walls derived using Brij-56 surfactant.

group (namely, the plane orientation with vertical or horizontal arrangement) cannot be excluded and may effect the interaction between the benzene molecules.

Further, upon calcination the materials do not show any significant change in benzene adsorption and the isotherm shapes match perfectly for the extracted and calcined materials (Figure 14b). No preferential change in the benzene adsorption upon calcination suggests a similar contact angle of adsorption or confirms the $\pi-\pi$ interaction between benzene moieties.

**Conclusion**

The hydrophobic mesoporous benzene-bridged organosilicas using biodegradable polyoxyethylene oligomers Brij-56 and Brij-76 surfactants were successfully synthesized under acidic conditions and characterized in detail. The materials are highly ordered, and the experimental results support the findings and provide the valuable information about the nature of the materials. Also in this work we have presented the first ever results on the physicochemical studies and adsorption properties of benzene-bridged mesoporous organosilicas with amorphous wall structures and compared them to the adsorption properties of benzene-silica carrying the molecular scale periodicity in the pore walls. The water and benzene adsorption results demonstrate the different textural behaviors for both kinds of materials.

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